CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
DEPARTMENT OF TOXIC SUBSTANCES CONTROL

HAZARDOUS WASTE TECHNOLOGY CERTIFICATION PROGRAM EVALUATION REPORT

Site Characterization and Analysis Penetrometer System Hydrosparge VOC Sensor
(SCAPS HS)
as an in-situ field screening technology
for the detection of selected volatile organic compounds in groundwater

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OCTOBER 2000

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Acronyms

1,1,2,2	1,1,2,2-tetrachloroethane
bgs	below ground surface
BRSA	Bush River Study Area
BTEX	benzene, toluene, ethyl benzene, and xylenes
CCl_4	carbon tetrachloride
$CHCl_3$	chloroform
CI	chemical ionization
CP	cone penetrometer
CPT	cone penetrometer truck
DCE	dichloroethene
DGCS	Davis Global Communication Site
DOD	Department of Defense
DTSC	California Department of Toxic Substances Control
ECB	Environmental Chemistry Branch
EI	electron impact
EPA	U.S. Environmental Protection Agency
FN	false negative
FP	false positive
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
HCl	hydrochloric acid
HS	Hydrosparge VOC Sensor
ITMS	ion-trap mass spectrometer
m/z	mass charge
min	minute
MMR	Massachusetts Military Reservation
NAS	Naval Air Station
OPPTD	Office of Pollution Prevention and Technology Development

Acronyms (cont.)

ORNL	Oak Ridge National Laboratory
PCE	perchloroethylene (tetrachloroethene)
PES	performance evaluation check standard
PFTBA	perfluorotributylamine
PQL	practical quantitation limit
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
QC	quality control
SCAPS	Site Characterization and Analysis Penetrometer System
SCAPS HS	SCAPS Hydrosparge
TCA	trichloroethane
TCE	trichloroethene (trichloroethylene)
USAEC	U.S. Army Environmental Compliance
USACE	U.S. Army Corps of Engineers
VOCs	volatile organic compounds
WES	Waterways Experimental Station

1   FORWARD

Section 25200.1.5, Health and Safety Code, enacted by Assembly Bill 2060, authorizes the Department of Toxic Substances Control (DTSC) to certify the performance of hazardous waste environmental technologies. The purpose of the certification program is to facilitate regulatory and end-user acceptance of environmental technologies and to promote and foster growth of California's environmental technology industry by providing an independent technical evaluation of technologies meeting applicable quality standards.

As part of this program, DTSC has evaluated a cone-penetrometer-based system for the on-site detection and characterization of specific chlorinated and aromatic chemicals in groundwater.   The developer of the technology is the U.S. Army Corps of Engineers (USACE), Waterways Experiment Station (WES), Vicksburgh, MS. This report was prepared to provide the results of this evaluation.

2   BACKGROUND

The Site Characterization and Analysis Penetrometer System (SCAPS) Hydrosparge (HS) VOC Sensor is a near real-time in-situ subsurface screening method for volatile organic compounds (VOCs) in groundwater. The technology was developed by the U.S. Army Corps of Engineers Waterways Experiment Station through the Tri-Service SCAPS program and is one of a planned family of sensors collectively called the Site Characterization and Analysis Penetrometer System, or SCAPS, that will combine remote sensors with a cone penetrometer platform to provide rapid, in-situ, subsurface measurements of many different contaminants.

 The conventional or traditional approach to characterizing groundwater contamination plumes depends on the installation of monitoring wells and collection of water samples followed by laboratory analyses, is usually a slow, iterative, and costly process. Significant delays occur in site characterization while samples are analyzed and new monitoring wells are being installed and developed. The SCAPS HS technology was designed to improve upon conventional site characterization by providing rapid qualitative to semi-quantitative information about the subsurface distribution of volatile organic contamination in groundwater.

3   TECHNOLOGY DESCRIPTION

The SCAPS Hydrosparge VOC Sensor consists of an in-situ sparge module interfaced to an ion trap mass spectrometer (ITMS) to provide near real-time semi-quantitative field screening analyses of volatile organic compounds (VOCs) in groundwater. The Hydrosparge VOC Sensor was developed for deployment with a standard cone penetrometer (CP) platform using a direct push groundwater sampling tool to create a temporary groundwater sampling point. Before the in-situ sparge module is lowered into the temporary sampling point or well, groundwater is purged until pH, dissolved oxygen, temperature, and conductivity remain constant and the groundwater level has been allowed to stabilize.

After being lowered into the sampling point or well through the push rods or casing, the in-situ sparge module uses an inert gas, helium, to purge or strip VOCs from the groundwater in module's sample chamber. The VOCs collected in the purge gas are then transferred to the surface via Teflon sampling tubing for direct real-time analysis by an on-board ion trap mass spectrometer.

The scope of evaluation focused on the use of the Hydrosparge VOC Sensor, including both the in-situ sparge module and the on-board ITMS, for near real-time analysis of selected VOCs in groundwater. The use of direct push sampling points or wells for field screening purposes is a generally accepted practice, and therefore was not evaluated. The evaluation specifically did not address the use of direct push sampling wells for obtaining representative groundwater samples, nor did it address any other uses of the CP system. This report provides a more detailed description of the CP platform and the direct push groundwater sampling tools that were used to aid the reader.

3.1   Hydrosparge Module

The hydrosparge module consists of a sparge chamber, a conductivity meter, a helium purge gas line connected to the sparging head, and a Teflon sample transfer line. A schematic of the hydrosparge module is shown in Figure 1. The hydrosparge module is lowered into a temporary groundwater monitoring well or sampling point. The conductivity meter in the sparge chamber ensures that the unit is placed approximately 18 inches below the groundwater surface. Groundwater enters the sparge chamber from an opening at the base of the hydrosparge module. Helium flows into the sparging head at a calibrated flow rate and sparges VOCs from the groundwater which are then released into a purge chamber. The helium and VOC vapors are sucked out of the top of the purge chamber via the sample transfer line. The sample transfer line is connected to the direct sampling ITMS. The helium flow rate into and out of the hydrosparge module is regulated by flow controllers located after the helium supply and prior to the ITMS, respectively. The hydrosparge module and ITMS are calibrated daily according to the described instrument operational procedure [7, 9].

3.2   Direct Sampling Ion Trap Mass Spectrometer

The ITMS, located within the SCAPS truck, is comprised of a sample inlet, a capillary restrictor interface, and a quadruple ion trap mass spectrometer. Unlike most mass spectrometry systems, the analyte vapors directly enter the ion trap mass spectrometer without being subjected to a separation technology such as a gas chromatograph. The presence of a selected ion mass in a series of scans is used for the identification and quantification of an individual or a specific class of compound. The ITMS and the In-Situ Hydrosparge Module were developed for application with the SCAPS by Oak Ridge National Laboratory (ORNL). Procedures for use of the Direct Sampling Ion Trap Mass Spectrometer (ITMS) are provided in U.S. EPA Draft Method 8265[7]. This method is currently under consideration by U.S. EPA for inclusion in their "Test Methods for Evaluating Solid Waste" (SW-846).

3.3   Support Platform and Cone Penetrometer (CP)

The SCAPS cone penetrometer platform is of commercially available design. Typically, the CP is housed in a 20-ton all-wheel drive truck with two compartments. One compartment, located over the truck's center of mass, contains a hydraulic ram used to push the cone penetrometer vertically into the ground. The other compartment within the truck houses computers for visualizing push data, equipment for controlling sample collection, and an ion-trap mass spectrometer for sample analysis. Figure 2 is a photograph of the SCAPS unit where the collapsible (accordion shaped) roof is located above the hydraulic ram.

The CP pushrod is composed of detachable 1- meter (m) long tubular sections which thread together one-by-one to lengthen the pushrod as it is advanced into the ground with a hydraulic ram against the weight of the truck. Typically, the CP sensors are advanced by attaching successive lengths of pushrod in 1-meter (m) lengths at a rate of up to 1 m per minute. The maximum depth of operation is governed by site-specific stratigraphy and the method is limited to sites where the cone penetrometer can be pushed to the depth of concern, through primarily unconsolidated sedimentary deposits or formations. Sites where cobbles or consolidated layers exist may prevent the penetration of the cone penetrometer or deflect the pushrods from a vertical path.

The SCAPS truck is also equipped with a steam cleaning system mounted underneath the truck. To avoid cross contamination between sampling locations, the CP pushrods are steam cleaned as they are withdrawn from the ground. The CP pushrods are pulled through a decontamination collar where two high pressure, high temperature water jets clean the pushrods as they are retracted from the ground. All decontamination water generated during steam cleaning is contained within the collar and diverted to a nearby collection container.

The water pump, heater, and storage tank for the steam cleaning system is located on a portable trailer attached to the rear of the SCAPS truck. This trailer also carries the slurry mixing bin and pump used to abandoned the temporary groundwater sampling points created using the direct push sampling tool.

3.4   Direct Push Sampling Tools

Hydropunch II™ and PowerPunch™ are examples of commercially available direct push sampling tools used to create a temporary groundwater sampling point or monitoring well. These tools can be attached to a push rod and advanced into the subsurface using the cone penetrometer rig. Hydropunch II™ is most effective in more permeable, unconsolidated formations. PowerPunch™ is used in less permeable formations where the groundwater recharges slowly.

Hydropunch II™ is equipped with a stainless steel drive point and stainless steel sleeve body. A schematic drawing of Hydropunch II™ is shown in Figure 1. The assembly is attached to the end of the CP pushrod and driven into the ground to the desired depth. The sleeve body and CP pushrods are

then pulled back to expose a 1.5-meter long section of ¾-inch diameter polyvinyl chloride (PVC) screen. No internal PVC riser pipe is attached to the PVC screen to extend it to the surface. The depth to groundwater is measured using a conductivity meter until the groundwater depth in the Hydropunch II™ is constant. The CP pushrods, functioning as the annular seal, remain in place until groundwater sampling is completed. Once sampling is completed, the sampling point is immediately grouted by lowering a _-inch diameter tube to the bottom of the push hole through the CP pushrod. The CP push rods are pulled up past the top of the well screen disconnecting the Hydropunch II™ screen and drive point. The tubing is then attached to the SCAPS slurry pump via quick-connect couplers. As the pushrods are retracted, a cement bentonite slurry is pumped into the abandoned screen. As each pushrod section is retracted, it is cleaned using the on-board steam-cleaning system. To remove a pushrod section, the slurry pump is stopped, and the tubing is disconnected at the quick-connect coupler. The quick-connect coupler is then re-connected and the slurry pump restarted for retraction of the next pushrod section. This process continues until the entire pushhole is filled with slurry from the bottom to the ground surface.

The standard PowerPunch™ tool is similar to the Hydropunch II™, except the PowerPunch™ is designed to allow PVC screen and blank casing to be attached to the drive point from the surface. Installing the PVC casing through the CP pushrods is similar to installing a well inside of a hollow-stem auger. By extending the PVC casing to the surface, the CP pushrods may be withdrawn while leaving the sampling point in place. A schematic diagram of the PowerPunch™ push tool is presented in Figure 3. The advantage of this system is that the SCAPS truck can be moved to another location while the groundwater recharges at the sampling point. Each sampling point is abandoned immediately after groundwater sampling is completed. The abandonment procedure for sampling points installed by PowerPunch™ is similar to the procedure described for Hydropunch™. The casing is detached from the drive point and the temporary well is then grouted from the bottom of the push hole to the ground surface by pumping a cement bentonite slurry through the PVC casing. Each section of the PVC casing is cleaned as it is withdrawn and then disconnected for storage.

4.0   EVALUATION OF TECHNOLOGY: GENERAL CONSIDERATIONS

The technology evaluation focused on the comparison of field results with those obtained using accepted reference methods for groundwater sampling and laboratory analyses. The performance parameters used to evaluate the technology included sensitivity, specificity, precision, accuracy, and reliability. These issues affect all field validations and are therefore discussed before a review of the validation studies.

4.1   Scientific Principles

The hydrosparge module operation is based on Henry's Law where for low concentrations of low-solubility VOCs in water, the concentration of the VOC in the gas phase is proportional to the

concentration in the water phase. For the hydrosparge gas flowrate used in the hydrosparge module, the VOC concentrations in the water phase remain relatively constant over the measurement time period. The purged VOCs are transferred directly to an on-site ion-trap mass spectrometer for analysis. Mass spectrometry in these validation studies was carried out either with a Teledyne 3DQ ITMS or with a Finnigan ITMS 40.

4.2   Hydrosparge Operation

The standard operating procedures for the in-situ measurement of VOCs in groundwater using SCAPS HS have been described in US EPA SW-846 Draft Method 8265 [7] , in *Current Protocol in Field Analytical Chemistry*, Field Screening of Volatile Organic Compounds Groundwater Using the Hydrosparge VOC Sensor[9], and in technology demonstration plans[4,5,17].

Hydrosparge module calibrations are performed to assess the system's performance. The following sections briefly describe system checks and calibration procedures used to make these assessments. The calibrations are run by placing the hydrosparge module in a 250 mL graduated cylinder containing the appropriate calibration solution.

4.2.1   Helium Flow Rate Adjustment

The helium flow rate of the sparging head can significantly affect the sensitivity. A slow purging rate can result in low detection sensitivity while a fast sample purging can result in splashing of water droplets into the sample transfer line. The proper helium flow rate is between 30 and 100 mL/min. Changes in the gas flow in the purging or transferring system require recalibration of the system. The flow rate of helium through the transfer line into the hydrosparge module is maintained slightly less than the helium flow rate from the module's purge chamber into the sample transfer line to ensure that the water is not accidentally sucked into the ITMS.

4.2.2   Analysis of Water Blank

After the helium flow rate is established, a water blank is run to establish a baseline. Internal standards are run with the initial water blank as a check for contamination due to carryover from the previous sample.

High level subsurface VOC contamination may present a problem for normal continuous operation. Interference from a previous sampling or residual VOC analytes remaining in the transfer lines may cause cross contamination between successive runs. Therefore, a water blank is also run between samples. It is especially important that a water blank be analyzed following a high level sample to ensure no carry over to the successive sample.

4.2.3 Performance Evaluation Check Standard

A performance evaluation check standard (PES) is used to check the instrument response. The PES standard contains acetone, dichloromethane, benzene, and bromobenzene to cover categories of compounds applicable to the method.

4.2.4 Quantitative Calibration

A calibration curve is developed by using laboratory standards containing known concentrations of the target analytes bracketing the desired concentration range. The internal standards are added to the target analytes for system calibration. The calibration curve is established by analyzing five different concentrations of standards in triplicate. A water sample blank simulating a ground water blank should be run for background subtraction. The water sample blank prepared by the WES consists of 148 mg/L of sodium sulfate and 165 mg/L of sodium chloride added to ASTM Type II water.

The acquisition time for the calibration is set to 30 minutes. A baseline signal from the water blank is acquired for 3 minutes, followed by data acquisition of the lowest standard solution. Data for each analyte are acquired for 2 minutes after the signal response has stabilized, when the total ion current becomes flat and horizontal, and steady state conditions have been achieved. When data acquisition has been completed, data acquisition is temporally halted and the probe removed from the solution. The probe is decontaminated by rinsing with distilled water before analysis of the next concentration standard.

4.2.5 Analysis of Groundwater

The hydrosparge module is placed in the water blank solution to obtain a baseline signal. Then, while continuing the data acquisition, the module is lowered through the cone penetrometer to the groundwater until the conductivity meter indicates that the proper depth has been achieved. A response for the analytes in the groundwater is observed after 45-120 seconds. Data is acquired for at least an additional two minutes after the response has stabilized. The hydrosparge module is then removed from the cone penetrometer for decontamination.

4.2.6 Decontamination and system check

The hydrosparge module is cleaned with deionized water, and the Teflon tubing is purged with helium gas. The hydrosparge module is then placed in the deionized water blank to ensure zero system response. Afterwards, the hydrosparge module is placed in a final spiked deionized water sample to check for proper system response. High concentrations of VOCs may sorb onto the sample transfer line, resulting in a false positive reading on the next sample. The technology is not intended for use where free-phase organics are present. If analytes are detected above the system background response, then the sample transfer line is purged with helium and the system rechecked with the

deionized water sample. If necessary, the sample transfer line may be replaced between samples.

4.2.7   Matrix Effects and Interferences

Non-target VOCs which generate an ion with the same mass/charge ratio as a target analyte may cause a positive interference.

4.3   ITMS Operation

Analysis of the SCAPS Hydrosparge (SCAPS HS) samples is performed with the use of a Teledyne 3DQ ITMS or Finnigan ITMS 40 operating in the electron impact mode or chemical ionization mode. The ITMS is directly fitted to a 20 cm DB-5 capillary column (ID100 μm, J&W part#160-2635) with restrictor heated interface operated at 105°C. The capillary interface limits flow into the ITMS at 0.1 to 1.0 mL/min., which is compatible with both electron impact (EI) and chemical ionization (CI) sources. The ITMS is operated in a full scan mode from masses 40 to 250 amu. Analyte identification is performed entirely by means of mass ion identification. Therefore, analytes with the same quantitation mass ions cannot be distinguished from each other and are reported as totals similarly to analytes co-eluting in gas chromatograph (GC) techniques.

4.3.1   Instrument Calibration and Data Acquisition

For daily operation, the mass spectrometer is checked and adjusted for the proper scan functions per instrument manufacturer's instructions.   The mass axis is calibrated with perfluorotributylamine (PFTBA) or bromofluorobenzene set in full scan mode. The mass spectra of air and water are evaluated for a system leak check. An instrument calibration file is acquired to ensure the proper setting of instrument tuning parameters. Other calibration and data acquisition activities are summarized in the hydrosparge module operation discussion above.

4.3.2   Method Detection Limit and Sensitivity

The SCAPS HS detection limit and quantitation limit are based on site-specific conditions. The ITMS ion intensity for each target analyte is measured in duplicate daily at the beginning of operations. The mean value of each concentration is used for calibration. For the least squares linear regression calibration curve, the intercept (b) is the intensity of unspiked water (background) and the slope (m) is the sensitivity of system response. The noise is defined as 2 times the standard deviation (s) of the fit. The ion intensity threshold given as the sum of the background and the noise values is the quantitation limit. The noise divided by the sensitivity is the detection level. With this approach the detection threshold varies from site to site but is generally in the range of 2 to 5 μg/L for the VOC analytes.

To increase the confidence level in the sensitivity near the detection threshold and to minimize the probability of false negatives, low concentration standards are used to establish the linear regression.

Samples above the linear calibration range of 1,000 µg/L are analyzed by reducing the ionization time during the data acquisitions with a corresponding reduction in the ionization time of the standards. Nonlinearity tends to occur at concentrations greater than a few mg/L in water.

4.3.3   Compound Identification and Quantification

Compound identification and quantitation are based on selected masses of each analyte. Quantitations of analytes are based on integration of a fixed number of scans, typically 80 to 100 scans, of the specific ions for a given analyte generated by either electron impact or chemical impact [7, 9]. The sample integration intervals should always be the same number of scans as that used for quantitation in the calibration. While the ion trap mass spectrometer is capable of detecting other compounds, its use with the hydrosparge module was only evaluated for the specific compounds specified in this evaluation report.

4.3.4   Sample Analysis

Samples were analyzed alternatively in EI and CI modes. Chlorinated solvents were detected by EI; benzene, toluene, ethyl benzene, and xylenes (BTEX) were detected by CI. The ITMS operated in a full scan mode from masses 40 to 250 amu.

4.3.5   Method precision and accuracy

Performance criteria and method recovery for ITMS are detailed in Draft EPA Method 8265. The ITMS has proven to be a stable detector once heated to operating temperature and calibrated. The method precision was estimated by analyzing standards in triplicate by placing the in-situ hydrosparge module into the spiked water sample.

Confirmation samples are collected and analyzed by standard methods such as Method 8260B. The fraction of samples that were confirmed by standard methods depends on site-specific factors such as the intent of the sampling, distribution of subsurface contamination, the number of positive and negative samples obtained by the SCAPS HS system, etc.

4.4   System Limitations

4.4.1   Sampling Depth

The sampling depth is typically limited by lithologic conditions at a site. Where lithologic conditions allow penetrations to deeper depths, the maximum sampling depth of the SCAPS HS is limited to the available length (200 ft.) of the umbilical cable which connects the hydrosparge module through the push rods to the SCAPS truck. Data used in this evaluation were generally from depths between 20 and 80 feet below ground surface (bgs). Thirteen samples were collected from greater than 100 feet bgs, with

one sample being at a depth of 184 feet bgs.

4.4.2   Groundwater Conditions

For all field studies reviewed for this report, the hydrosparge module was operated at 18-inches below the groundwater surface of the well. The conductivity meter on the hydrosparge module is set for that depth. The Henry's Law equilibrium concentration of VOCs between the vapor and aqueous phases is pressure dependent. Since data are not available to assess the hydrosparge module's ability to profile vertical contaminant loading, the unit was not evaluated for such a capability and its use is limited to 18-inches below the groundwater surface for purposes of this evaluation.

The hydrosparge module may be affected by the amount of silt present in the groundwater. Since the sampling point installed using the CPT and direct push sampling tool has no sand pack in place, the sampling point is subject to "silting in" when operated in the presence of high silt groundwater. "Silting in" may partially or completely block the PVC screens impeding the groundwater flow into the sampling point.

4.4.3   Lithologic Conditions

The system can only be operated where the SCAPS CP can reach the desired depth. Cobbles or consolidated layers may prevent the penetration of the SCAPS penetrometer or deflect it from a vertical path. The system may also be limited by low hydraulic conductivity aquifers which require a longer time for the groundwater level to stabilize.

4.4.4   Limitation to Known Contaminants

Since the ITMS does not have a separation mechanism other than the mass spectrometer, compounds which produce identical primary characteristic ions, or positional and geometric isomers (e.g., 1,1-dichloroethene and 1,2-dichloroethene), cannot be positively identified by this system unless a characteristic secondary ion is available for monitoring. Compounds with higher molecular weights may produce the same fragment ions which will increase the signal of target analytes.   A false positive result may occur when VOCs are present in the sample which yield molecular ions or ion fragments with the same mass/charge (m/z) values as the characteristic ions of the target VOCs. Therefore, this detection system can only be used to detect or confirm the presence of target analytes but not for the positive identification of unknown compounds.

4.5   Reliability

The USACE has reported deployment of the SCAPS HS system at 6 hydrogeographic locations with over 194 penetrations. Data has been collected from groundwater contaminated with chlorinated

VOCs and BTEX. In addition, the SCAPS HS has been deployed at over 25 sites by the Tulsa, Savannah, and Kansas City Army Corp of Engineer Districts.

4.6   Performance Claims used as Basis for Evaluation Scope

WES provided performance claims to use as the basis for the evaluation. These claims allowed DTSC to identify a scope and data needs for the evaluation.

The original Hydrosparge VOC Sensor claims are as follows:

1.   Using the prescribed technology and its prescribed 5 point linear calibration curve ($R^2 \geq$ 0.95), the method estimates the concentration of individual VOC analytes in groundwater in the range of 3 µg/L to 10 mg/L to within ±20%.

2.   At the nominal action level of 5µg/L for individual analytes, the method correctly estimates the concentration 90% of the time with less than 5% false negatives and 5% false positives.

3.   Over the range of 3µg/L to 10 mg/L, SCAPS HS results correlate linearly ($R^2 \geq 0.80$) with results obtained by EPA Method 8260 for groundwater samples obtained from the direct push sampling point.

4.6.1   The Probabilities of False Positive (FP) and False Negative (FN) Results

False positive or negative results may occur due to variability in the groundwater matrix, due to the variability inherent in each analytical method, or due to differences between the analytical methods (ion trap mass spectrometry for the ITMS and gas chromatography/mass spectrometry for EPA Method 8260B). As a field screening tool, the false negative rate is of interest. Failure to detect a contaminant that is present could have an adverse impact on site or public health management decisions. False positive results may occur for compounds with the same m/z ratio values as other VOCs. The USACE proposed that at the action level of 5 µg/L for individual VOCs, the method would correctly estimate the concentration 90% of the time with 5% or less false positives and 5% or less false negative results. Determination of false positive and false negative rates is complicated by the variability inherent in the reference method. To provide data on this variability during the field tests, some samples were split and sent for analysis by a second, independent laboratory.

For this certification evaluation, false positives and negatives were determined with respect to the detection limits for the HS analyses and the corresponding confirmation samples (Method 8260B analyses). Rules for determining confirmed positives and negatives, and false positives and negatives were as follows:

Confirmed Positive (+/+). In confirmed positives, the SCAPS HS and confirmation sample

analyses detected an analyte above their respective detection limits.

Confirmed Negative (-/-). In confirmed negatives, the analyte was not detected with the SCAPS HS method or the confirmation sample analysis, or was detected with the SCAPS HS method below the detection limit of the confirmation sample.

False Positive (+/-). In false positives the analyte was detected with the SCAPS HS method but was not found to be present in the confirmation sample above the detection limit of the SCAPS HS method.

False Negative (-/+). In false negatives, the analyte was not detected with the SCAPS HS method but was found to be present in the confirmation sample at or above the detection limit of SCAPS HS method.

Section 7.0 summarizes the percentage false negative and false positive results achieved for the field studies reviewed for this certification evaluation. Based on the results and reported detection levels for the SCAPS HS in-situ samples and EPA Method 8260B, the SCAPS HS method correctly reported the presence or absence of TCE, benzene, carbon tetrachloride, PCE, toluene, and xylenes better than 90% of the time with less than or equal to 5% false positives and less than or equal to 5% false negative results.

4.7   Description of Sampling for Analyses by Reference Method, EPA Method 8260B

In general, a confirmation (reference method) sample is collected for each SCAPS HS sample collected. When the groundwater level in the temporary groundwater sampling point has stabilized, the sampling point is bailed with a small diameter teflon bailer until the bailed groundwater sample yields a constant pH, dissolved oxygen, temperature, and conductivity. The pH, dissolved oxygen, and conductivity are measured in the field using Standard Methods for Examination of Water and Wastewater Methods 423 and 205, respectively. Prior to collecting each SCAPS HS sample, a confirmation sample is collected using a teflon bailer. Groundwater from the bailer is placed in precleaned 40 mL VOA vial, preserved with 3 drops of concentrated hydrochloric acid (HCl) and sealed with a teflon lined cap. Following collection and until analysis, all confirmation samples are stored on ice in coolers at approximately 4°C.

5   TECHNOLOGY EVALUATION: PREVIOUS STUDIES BY WES

The U.S. Army Environmental Center (USAEC), USACE tested the SCAPS HS at four Department of Defense (DOD) facilities, without DTSC oversight, to demonstrate the system's performance in comparison to conventional sampling and analytical methods. The sites were (1) Building 525 at Aberdeen Proving Ground, Maryland; (2) Bush River Study Area at Aberdeen Proving Ground, Maryland; (3) Massachusetts Military Reservation; and (4) Naval Air Station Whiting Field, Florida.

USACE submitted summary reports of these studies in support of their claims and to provide background for the field studies that were conducted.   Each of these field studies are discussed below. A summary of individual sample results by field study is provided in Appendix A.

5.1   Building 525, Aberdeen Proving Ground, Maryland

Building 525 was used for cleaning and painting of vehicles and weapons systems. Solvents and petroleum products had been detected in the groundwater near the building during site investigations. The USACE reported that the site stratigraphy investigations found surficial fill in some areas beneath which was clay, silt and silt/clay mixes to a depth of 10 to 15 feet bgs[18]. Below that depth, sand and sand/gravel mixes with narrow interbedded clay and silt/clay lenses were encountered down to 25 to 30 feet bgs. The depth to the first groundwater aquifer, assumed to be unconfined, was generally 12 to 15 feet bgs. This aquifer extends to about 30 feet bgs, and is probably connected to a second aquifer from 30 to 50 feet bgs.

In August 1995, the USACE completed 23 samples with the SCAPS HS at 22 locations near the building. The samples were collected from direct push sampling points with a four-foot screen interval. The center of the screen intervals were between 13 and 20 feet bgs, except for one location where samples were collected at 43 and 68 feet bgs. After completing the SCAPS HS measurement, a bailer was used to collect three 40 mL VOA vials. The VOA vials were shipped to an analytical laboratory for confirmatory analysis by reference method, EPA Method 8260B. The penetrometer pushrods were then retracted and the hole grouted. The analytes reported were trichloroethene (TCE) and trichloroethane (TCA).

Analytes	Number of GW Samples		Sample Result Distribution				r^2	Detection Limit (ng/mL)		EPA Method 8260 Confirmation Sample Max. Conc.	true +		true -		false +		false -	
	Hydrosparge	Confirmation	n<5	5<n<100	100<n<1000	n>1000		Method 8260	Hydrosparge	(ng/mL)	Number	%	Number	%	Number	%	Number	%
TCA	23	23	7	11	4	1	1.0	<5	<5	1300	15	65%	5	22%	2	9%	1	4%
TCE			7	5	10	1	1.0	<5	<5	1200	14	61%	4	17%	3	13%	2	9%

As listed in Table 1 above, TCA concentrations ranged from non-detect (< 5 µg/L) to 1,300 µg/L. Seven data points had concentrations below the detection limit, 11 data points were between 10 and 100 µg/L, and 5 data points were greater than 100 µg/L. False positives were 9% (or 2 out of 23 samples) while false negatives were 4% (or 1 out of 23 samples). The small number of samples makes this of limited statistical value because a few false positives or negatives can result in failure to meet the criteria. False positives were reported by the SCAPS HS method at 17 µg/L (HS04) and 6 µg/L (HS23) while the reference method listed non-detects for these samples. The false negative, associated with sample HS06, had a 12 µg/L reported by the reference method while the SCAPS HS method reported non-detect. The results for the two methods correlated well (R^2=0.98) even though the number of data points were limited. A plot of the SCAPS HS results versus the reference method

results is presented in Figure 4.

As shown in Table 1 above, TCE concentrations ranged from non-detect to 1,200 µg/L. Seven data points had concentrations below the detection limit, 5 data points were between 5 µg/L and 100 µg/L, and 11 data points were greater than 100 µg/L. False positive rates were 13% and false negatives were 9%. The false positives were reported at 10 µg/L (HS04), 59 µg/L (HS23), and 34 µg/L (HS25) by the SCAPS HS method and as non-detect by the reference method. One false negative was reported at 7.7 µg/L by the reference method while the SCAPS HS reported non-detect. For sample HS09A, TCE was reported below the detection limit by both methods, but detected at 12µg/L in a duplicate sample (HS09B) by the reference method. Since limited information was available on this field study, Office of Pollution Prevention and Technology Development (OPPTD) staff could not determine the cause of the difference between the sample and its duplicate. The results for the two methods correlated well (R^2=0.95) even though the number of data points were limited. These results are plotted and presented in Figure 4.

5.2   Aberdeen Proving Ground, Bush River Proving Grounds (BRSA), Maryland

According to USAEC, the BRSA has been used for training, test activities, disposal, and chemical storage[17]. Groundwater is contaminated with petroleum hydrocarbons and chlorinated solvents. The stratigraphy is complex, with interbedded clay, silt, sand, and gravel. The groundwater surface is found at 8 to 13 feet bgs, and forms an upper aquifer 2 to 29 feet thick. The upper aquifer is unconfined or, in places, semi-confined. A deeper, confined aquifer is separated from the upper aquifer by a confining layer.

During June and August 1996, 31 direct push temporary wells were sampled at one to three depths each, and three existing wells were sampled at one depth each, for a total of 82 SCAPS HS results. For each SCAPS HS result, a bailed sample was submitted to an off-site laboratory for confirmation analysis by the reference method, EPA Method 8260B. SCAPS HS and EPA Method 8260B results were reported for TCE, tetrachloroethene (PCE), carbon tetrachloride (CCl_4), a mixture of dichloroethene/trichloroethane (DCE/TCA), and a mixture of chloroform/1,1,2,2-tetrachloroethane ($CHCl_3$/1,1,2,2). ITMS could not distinguish between DCE and TCA, and between $CHCl_3$ and 1,1,2,2, so USACE reported these results as a mixture of the two compounds. Since the two chemicals in each pair have different relative responses in the ITMS, this must be taken into account when comparing SCAPS HS and reference method results.

The results for the June and August demonstrations have been grouped by analyte or analyte mixture and discussed in the paragraphs below. A summary of the sample results and data analysis for the two demonstrations is provided in Table 2. Combined results for the June and August demonstrations for the SCAPS HS method versus the reference method are plotted and presented in Figure 5. Figures 6 and 7 provide separate plots of the June and August 1996 demonstration data.

Analytes	Number of GW Samples		Sample Result Distribution				r²	Detection Limit (ng/mL)		EPA Method 8260 Confirmation Sample Max. Conc. (ng/mL)	true +		true -		false +		false -	
	Hydrosparge	Confirmation	n<5	5<n<100	100<n<1000	n>1000		Method 8260	Hydrosparge		Number	%	Number	%	Number	%	Number	%
August 1996																		
1122 +CHCL3	19	19	7	4	2	6	0.6	<5	<5	6870	9	47%	4	21%	3	16%	3	16%
DCE+TCA			12	6	1	0	0.6	<5	<5	159	6	32%	11	58%	1	5%	1	5%
CCL4			11	4	4	0	0.9	<5	<5	590	8	42%	10	53%	1	5%	0	0%
PCE			17	2	0	0	0.4	<5	<5	34	2	11%	14	74%	3	16%	0	0%
TCE			13	1	5	0	0.9	<5	<5	640	6	32%	12	63%	1	5%	0	0%
June 1996																		
1122 +CHCL3	63	63	22	23	13	5	0.6	<5	<5	8970	28	44%	21	33%	1	2%	13	21%
DCE+TCA			56	6	1	0	0.3	<5	<5	132	5	8%	53	84%	3	5%	2	3%
CCL4			49	11	3	0	0.2	<5	<5	370	13	21%	47	75%	1	2%	2	3%
PCE			54	8	1	0	0.0	<5	<5	820	7	11%	51	81%	2	3%	3	5%
TCE			40	17	6	0	0.7	<5	<5	830	16	25%	39	62%	2	3%	6	10%

Referring to Table 2 above, concentrations for the 1,1,2,2/CHCL3 mixture ranged from non-detect to 8,970 µg/L. Twenty-nine data points had concentrations below the detection limit, 27 data points were between 5 µg/L and 100 µg/L, and 26 data points were greater than 100 µg/L. False positives ranged from 2% to 16%, and false negatives from 16% to 21%. False negatives associated with the June 1996 demonstration had reference method values ranging from 6.4 to 160 µg/L while SCAPS HS values were non-detect. False negatives for the August 1996 demonstration had concentrations ranging from 68 to 1300µg/L for the reference method while the corresponding SCAPS HS results were non-detect. Correlation of the SCAPS HS data with the reference method was poor for both demonstrations when plotted separately or combined (R^2<0.6). When sample SBRBH2 was omitted from the June 1996 data set, correlation for 1,1,2,2/CHCL3 results improved to R^2>0.8.

Concentrations for the DCE/TCA mixture ranged from non-detect to 159 µg/L. Sixty-eight data points had concentrations below the detection limit, 12 data points were between 5 µg/L and 100 µg/L, and 2 data points were greater than 100 µg/L. False positives were 5% and false negatives ranged from 3% to 5%. False positives identified by the SCAPS HS method for the June 1996 demonstration ranged from 5 µg/L to 6 µg/L while the reference method reported non-detect. For the August 1996 demonstration, one false positive was reported at 18 µg/L for sample SBR37H02 by SCAPS HS method and as non-detect by the reference method. False negatives for the June 1996 demonstration had values of 132 µg/L (SBRBH2) and 92 µg/L (SBRKH2) for the reference method while corresponding SCAPS HS values were non-detect. For the August 1996 demonstrations, the false negative for sample SBR44H02 was reported by the reference method at 7 µg/L and as non-detect by the SCAPS HS method. Correlation of the data with the reference method was poor for both the individual field studies and the pooled data (R^2≤0.6).

CCl₄ concentrations ranged from non-detect to 590 µg/L. Sixty data points had concentrations below the detection limit, 15 data points were between 5 µg/L and 100 µg/L, and 7 data points were greater than 100 µg/L. False positives ranged from 2% to 5% and false negatives ranged from 0% to 3%. The false positive for the June 1996 demonstration was associated with sample SBR30H1 where the

SCAPS HS method value was 4.9 µg/L while the reference method value was non-detect. For the August 1996 demonstration, the SCAPS HS method reported a false positive value of 38 µg/L for sample SBR38H03. False negatives for the June 1996 demonstration were reported by the reference method at 24 µg/L and 5 µg/L for samples SBR21H2 and SBR30H2, respectively. Data correlation between the field results and the reference method varied from poor (R^2=0.2) to good (R^2=0.9) between the June 1996 and August 1996 demonstrations. Insufficient information was available to identify potential causes for these differences. When the data was pooled, a good correlation (R^2=0.8) was observed between the field results and the reference method.

PCE concentrations ranged from non-detect to 820 µg/L. Seventy-one data points had concentrations below the detection limit, 10 data points were between 5 µg/L and 100 µg/L, and 1 data points were greater than 100 µg/L. For both demonstrations, false positives varied from 3% to 16% and false negatives from 0% to 5%. For the June 1996 demonstration, a false positive was reported for sample SBRBH1 where the SCAPS HS detected 34 µg/L and the reference method non-detect. False positives for the August 1996 demonstration had SCAPS HS results of 44 µg/L (SBR38H03), 21 µg/L(SBR42H01), and 20 µg/L (SBR45H01) while the corresponding reference method results were non-detect. False negatives for the June 1996 demonstration were 7.5 µg/L (SBR21H2), 5.3 µg/L (SBR22H1), and 41 µg/L (SBRKH2A) for the reference method and non-detect for the SCAPS HS method. The small size of the data set (19 points) for the August 1996 demonstration makes this of limited statistical value because a few false positives or negatives can result in failure to meet the criteria. Correlation for both demonstrations were poor (R^2<0.4) but due to the limited amount of information available, the cause for the low correlation was not identified.

TCE concentrations ranged from non-detect to 1,200 µg/L. Fifty-three data points had concentrations below the detection limit, 18 data points were between 5 µg/L and 100 µg/L, and 11 data points were greater than 100 µg/L. TCE results had false positives between 3% to 5% and false negatives between 0% to 10%. False positives were associated to samples SBR18H1 and SBR18H2 for the June 1996 demonstration, and sample SBR37H02 for the August 1996 demonstration. The SCAPS HS method reported concentrations at 7 µg/L (SBR18H1), 6 µg/L (SBR18H2), and 20 µg/L (SBR37H02) while the reference method values were non-detect. For the June 1996 false negatives, the reference method reported values of 12 µg/L (SBR01H3), 5.4 µg/L(SBR30H3), 12 µg/L (SBR31H1), 40 µg/L (SBR32H2), 33 µg/L (WBR19), and 41 µg/L (SBRMH1) while the SCAPS HS method reported non-detects. For two demonstrations, the correlation was poor for the June 1996 demonstration (R^2=0.7) yet good correlation (R^2>0.8) was achieved for the August 1996 demonstration. Since field notes were not available for review, it is difficult to determine the field factors which may have contributed to the differing correlations. An example of possible factors include operator errors such as omission of dilution factors or transcription errors.

5.3   Naval Air Station (NAS) Whiting Field, Florida

NAS Whiting Field is a fixed-wing aircraft and helicopter training base, with associated support facilities. Contaminants at the site include chlorinated solvents and petroleum hydrocarbons from an underground waste solvent storage area, an aviation gasoline tank sludge disposal area, and an open burning and disposal area. The stratigraphy consists of sand, clayey silt and silty clay interspersed with clay and gravel lenses, beds and stringers. Cone penetrometer penetrations were completed to depths ranging from 64 to 243 feet bgs, while hydrosparge measurements were taken at depths between 87 and 184 feet bgs. An initial push with a conventional CPT probe was completed at each sampling location to define soil stratigraphy and dynamic pore pressures. A separate push was completed for each groundwater sampling depth identified using the CPT probe. Five locations with measurements at one to three depths per location were taken with both the hydrosparge and EPA Method 8260B, for a total of nine determinations. Results were reported for benzene, toluene, xylene, DCE, PCE, and TCE[20].

The range of analyte concentrations for this study did not span more than one order of magnitude except for TCE. The maximum concentration for each analyte is listed in Table 3. False positives were below the 5% performance criteria for all analytes. False negatives were below the 5% performance criteria for all analytes except DCE and TCE which were at 10%. The false negative for DCE was associated with sample STP02HS02 where SCAPS HS did not detect DCE and the reference method detected it at 11µg/L. SCAPS HS detected TCE in sample CPT01HS02 at 2µg/L while reference method detected it at 5µg/L. The small size of the data set (9 points) makes this of limited statistical value because a few false positives or negatives can result in failure to meet the criteria. The false negative for TCE could be counted as a true positive since the SCAPS HS reported an estimated value. Since the concentration ranges for most analytes (except TCE) were narrow, the regression analysis for these analytes were either not performed or presented for informational purposes only. As shown in Figure 8, good correlations were obtained for TCE and toluene (R^2=0.9), with lower correlations for DCE and benzene (R^2=0.6).

Analytes	Number of GW Samples		Sample Result Distribution				r^2	Detection Limit (ng/mL)		EPA Method 8260 Confirmation Sample Max. Conc. (ng/mL)	true +		true -		false +		false -	
	Hydrosparge	Confirmation	n<5	5<n<100	100<n<1000	n>1000		Method 8260	Hydrosparge		Number	%	Number	%	Number	%	Number	%
BENZENE	9	10	9	0	0	0	0.6	<5	<5	(2)	0	0%	9	100%	0	0%	0	0%
TOLUENE			8	1	0	0	0.9	<5	<5	6	1	11%	8	89%	0	0%	0	0%
XYLENES			9	0	0	0	–	<5	<5	ND	0	0%	9	100%	0	0%	0	0%
DCE			7	2	0	0	0.6	<5	<5	16	1	11%	7	78%	0	0%	1	11%
PCE			9	0	0	0	–	<5	<5	ND	0	0%	9	100%	0	0%	0	0%
TCE			7	0	2	0	0.9	<5	<5	170	2	22%	6	67%	0	0%	1	11%

5.4 Massachusetts Military Reservation (MMR)

During January 1996, the SCAPS HS was deployed at the MMR. MMR is a base overlying Cape Cod's major groundwater aquifer. The lithology consists primarily of various size sands. At the locations where the SCAPS HS was deployed, the depth to groundwater was 74 to 85 feet bgs. Potential waste sources at MMR are associated with aircraft and vehicle maintenance, landfills, stormwater runoff, and firefighter training activities. Groundwater contaminants at the site include halogenated solvents and fuel hydrocarbons. A dummy tip was required on several penetrations to break through a one-foot thick consolidated sand layer just above the groundwater surface. Once that layer was penetrated, the penetrometer could easily be pushed to greater depths. At some other locations on the base, the SCAPS probe was unable to penetrate beyond 20 feet due to the presence of cobbles. Four penetrations were successfully completed at the base, for a total of eleven measurements. At one penetration location, a single measurements was taken with a screen interval centered at a depth of 93 feet bgs, at another penetration location, measurements were performed at 79, 94, 109, and 123 feet bgs, at the third location, five measurements were taken at depths of 79, 94, 109, 124, and 146 feet bgs, and at the fourth location a single measurement was taken at a depth of 82 feet bgs[19]. Analytes included DCE, TCE, PCE, $CHCl_3$, benzene, toluene, and xylenes.

Analyte concentrations did not span more than one order of magnitude with some analytes not detected in any samples by either method. The maximum concentration, and false positive and negative percentages is presented in Table 4. No false positives or negatives were reported for any of the analytes except DCE which had 9% false positives. DCE, TCE, and PCE were detected in one sample (MMR-HP10) by the SCAPS HS method at 1.53 µg/L (DCE), 1.11 µg/L (PCE), and 16.94 µg/L (TCE). EPA Method 8260B results reported TCE at 14 µg/L and 1 µg/L of PCE in this sample, but did not detect DCE. In sample MMR-HP11, $CHCl_3$ was detected at 1.45 µg/L by both the SCAPS HS method and at 2.6 µg/L by EPA Method 8260B. None of the target analytes were detected in the other nine samples. Due to the narrow concentration range and small data set, a regression analysis was not performed.

Analytes	Number of GW Samples		Sample Result Distribution				r^2	Detection Limit (ng/mL)		EPA Method 8260 Confirmation Sample Max. Conc. (ng/mL)	true +		true -		false +		false -	
	Hydrosparge	Confirmation	n<5	5<n<100	100<n<1000	n>1000		Method 8260	Hydrosparge		Number	%	Number	%	Number	%	Number	%
DCE	11	11	11	0	0	0	--	<1	<1	ND	0	0%	10	91%	1	9%	0	0%
TCE			10	1	0	0	NA	<1	<1	14	1	9%	10	91%	0	0%	0	0%
PCE			11	0	0	0	NA	<1	<1	1	1	9%	10	91%	0	0%	0	0%
CCL4			11	0	0	0	--	<1	<1	ND	0	0%	11	100%	0	0%	0	0%
1122+CHCL3			11	0	0	0	NA	<1	<1	2.6	1	9%	10	91%	0	0%	0	0%
BENZENE			11	0	0	0	--	<1	<1	ND	0	0%	11	100%	0	0%	0	0%
TOLUENE			11	0	0	0	--	<1	<1	ND	0	0%	11	100%	0	0%	0	0%
XYLENES			11	0	0	0	--	<1	<1	ND	0	0%	11	100%	0	0%	0	0%

6 TECHNOLOGY EVALUATION: CERTIFICATION FIELD DEMONSTRATIONS

A field test, consisting of two field demonstrations, was conducted by WES with oversight by DTSC at the Davis Global Communications Site (DGCS), part of McClellan Air Force Base, California. Another field test was conducted at Fort Dix, New Jersey, with oversight by the New Jersey Department of Environmental Protection. A summary of individual sample results for each field test is provided in Appendix A.

For both the DGCS and Fort Dix field tests, the sampling procedure discussed in Section 4.7 was followed to collect confirmation samples. Prior to each SCAPS HS sampling and analysis, a confirmation sample was collected using a Teflon bailer. Groundwater from the bailer was placed in precleaned 40 ml VOA vials, sealed with Teflon lined caps, and stored in coolers on ice at approximately 4°C. Samples were preserved with 3 drops of concentrated HCl except for those sent to the WES which were to be analyzed within 7 days after collection and did not require preservation. After taking the confirmation sample, the Hydrosparge module was lowered into the temporary sampling point, 18 inches below the groundwater surface, to perform the SCAPS HS analysis.

Confirmation samples were collected in triplicate. One of these replicates was shipped to an independent laboratory for analyses. Two of the replicates were shipped to WES's Environmental Laboratory. One of the duplicates was analyzed while the other served for QA/QC purposes, or to resolve any questions concerning sample integrity that may arise. Five percent of the confirmation samples were also analyzed in triplicate for QC purposes. These samples were also immediately stored on ice for shipment to the off-site laboratory for analysis by EPA Method 8260B.

6.1 Davis Global Communications Site (DGCS), McClellan Air Force Base, CA

The DGCS annex of McClellan AFB consists of a main compound area, communication antennas and undeveloped grasslands. Contamination at the site resulted from releases of halogenated solvents and hydrocarbon fuels during storage and maintenance activities at the site. The lithology consists primarily of fine grained sands, silts and silty clays of flood plain origin. Gravel and sand lenses are also present. Groundwater fluctuates seasonally with rainfall, primarily between November and March, and with agricultural pumping from late spring until early fall. During winter months the groundwater surface fluctuates between approximately 25 to 35 feet bgs, while in summer months it fluctuates between approximately 60 to 70 feet bgs.

WES performed a field test consisting of two field demonstrations conducted in November/December 1996 and February 1997. The target analytes for both demonstrations using the SCAPS HS included PCE, TCE, and DCE. Confirmation samples were collected from Powerpunch™ groundwater sampling points, and submitted to the WES's Environmental Laboratory for analysis by U.S. EPA Method 8260B. The sampling procedure used for both demonstrations is described in Section 6.0. The lower reporting limit for the Method 8260B results was 5µg/L; several values below this

concentration were reported as estimated concentrations (J values).

In November/December 1996, a total of ten Powerpunch™ sampling points were installed near existing monitoring wells with each sampling point screened over the same intervals as the existing wells (generally between 60 to 80 ft bgs). For each groundwater sampling point, the hydrosparge module was used to obtain a SCAPS HS analysis and then a bailed confirmation sample was obtained for off-site analysis. The sampling procedure described in Section 6.0 was followed except the confirmation samples were collected after the SCAPS HS samples[6].

Replicate confirmation samples were shipped to West Laboratory, an independent accredited laboratory in California, as a quality assurance/quality control (QA/QC) check for the November/December 1996 demonstration. The additional samples were collected from groundwater sampling points adjacent to monitoring wells DMW03 and DMW06. The results for these samples are shown in Figure 9 and Table 5. Comparison of the SCAPS HS and ECB results showed good data correlation (R^2=0.9) while the West Laboratory results correlated poorly with the SCAPS HS and ECB results (R^2=0.6).

	TCE (ug/L)			DCE (ug/L)			PCE (ug/L)		
Sample	HS[1]	ECB[2]	PDP[3]	HS[1]	ECB[2]	PDP[3]	HS[1]	ECB[2]	PDP[3]
DMW03H03	0	0	0	0	0	0	0	4.3	1.1
DMW03H03	5	19	16	5	5.7	5.6	117	170	76
DMW06H02	109	243	76	61	45	39	213	253	44
DGCSH21	88	74	56	19	19.7	29.8	49	43	34
DGCSH23	15	19	18	2	2.3	5.7	20	23	22
DGCSH28	60	50	40	39	8	12.9	298	383	70

1 - SCAPS Hydrosparge/Ion Trap Mass Spectrometry
2 - Environmental Chemistry Branch, Waterways Experimental Station, U.S. Army Corp of Engineers Method 8260
3 - West Laboratory, an Independent Laboratory

For the February 1997 demonstration, an additional 22 Powerpunch™ groundwater sampling points were completed at various locations. The Powerpunch™ sampling points near DMW06 were screened over the same interval as monitoring well DMW06. This demonstration followed the sampling procedure described in Section 6.0 with no known deviations.

The results for the two demonstrations are summarized in Table 6 below. Regression analysis for TCE, DCE and PCE for the combined results from the two demonstrations is presented in Figure 10. The regression analysis for each individual demonstration is presented in Figure 11.

DCE concentrations ranged from non-detect to 61 µg/L where 13 data points had concentrations below the detection limit, 19 data points were between 5 µg/L and 100 µg/L, and no data points were greater than 100 µg/L. False positives were 0% for both demonstrations while false negatives ranged from 0%

to 9%. The two false negatives for the February 1997 demonstration were reported at 4µg/L (sample DMW06H09) and 2µg/L (sample DGCSH24) by the SCAPS HS method and at 9µg/L by the reference method for both samples. These false negatives could be counted as true positives since the SCAPS HS method reported an estimated value. When the results for the two demonstrations were combined, the correlation was poor ($R^2=0.6$). When the November/December 1996 results were plotted separately, the correlation was good ($R^2=0.9$) while the February 1997 results correlated poorly ($R^2=0.4$). The sampling reports for the both events did not provide enough information to identify the site conditions which may have contributed to the lower correlations in February 1997.

TCE concentrations ranged from non-detect to 240 µg/L where 7 data points had concentrations below the detection limit, 22 data points were between 5 µg/L and 100 µg/L, and 3 data points were greater than 100 µg/L. No false positives were found in the data for both demonstrations while false negatives were 0% and 5%. The false negative was associated with sample DGCSH35 where the concentration was reported as non-detect by SCAPS HS and at 9µg/L by the reference method. When the results for the two demonstrations were combined, the correlation was good ($R^2=0.9$). When the results for the demonstrations were plotted separately, the November/December 1996 results correlated well ($R^2=1.0$) while the February 1997 results correlated poorly ($R^2=0.7$). If sample DMW06H08 is omitted from the February 1997 data set, then the correlation coefficient increases from $R^2=0.7$ to $R^2=0.9$. Since the February 1997 sampling report did not provide enough information on field activities, OPPTD could not determine if this point was an outlier.

PCE concentrations ranged from non-detect to 820 µg/L where 5 data points had concentrations below the detection limit, 16 data points were between 5 µg/L and 100 µg/L, and 11 data points were greater than 100 µg/L. False positives and negatives were reported for the February 1997 demonstration at 5% and 9%, respectively. The one false positive (sample DGCSH29) was detected by the SCAPS HS method at 9µg/L and as non-detect by the reference method. The two false negatives were detected at 220µg/L (sample DGCSH26) and 11µg/L (sample DGCSH35) by the reference method and as non-detect by the SCAPS HS method. When the results from the two demonstrations were combined, good correlation ($R^2=0.9$) was observed between data obtained by the reference method and SCAPS HS method. When the results for the two demonstrations were plotted separately, the November/December 1996 results correlated well ($R^2=1.0$) while the February 1997 results correlated poorly ($R^2=0.6$). If sample DGCSH26 is omitted from the data set, then the February 1997 results correlate well ($R^2=0.8$). The February 1997 sampling report did not provide information on the field activities for OPPTD to determine if this point should be rejected as an outlier.

Analytes	Number of GW Samples		Sample Result Distribution				r^2	Detection Limit (ng/mL)		EPA Method 8260 Confirmation Sample Max. Conc. (ng/mL)	true +		true -		false +		false -	
	Hydrosparge	Confirmation	n<5	5<n<100	100<n<1000	n>1000		Method 8260	Hydrosparge		Number	%	Number	%	Number	%	Number	%
February 1997																		
DCE	22	22	9	13	0	0	0.4	<5	<5	61	12	55%	8	36%	0	0%	2	9%
PCE			3	14	5	0	0.6	<5	<5	240	17	77%	2	9%	1	5%	2	9%
TCE			4	17	1	0	0.7	<5	<5	384	17	77%	4	18%	0	0%	1	5%
November/December 1996																		
DCE	10	10	4	6	0	0	0.9	<5	<5	48	8	80%	2	20%	0	0%	0	0%
TCE			3	5	2	0	1.0	<5	<5	220	7	70%	3	30%	0	0%	0	0%
PCE			2	2	6	0	1.0	<5	<5	640	6	60%	4	40%	0	0%	0	0%

6.2   Fort Dix, New Jersey

Fort Dix is used for military training activities. Potential sources of groundwater contamination include landfills, underground storage tanks, and motor pools and vehicle repair areas. Groundwater VOC contaminants include halogenated solvents (e.g., TCE, DCE) and fuel hydrocarbons (e.g., benzene, toluene, xylenes).

During June 1997 a total of 32 Powerpunch[TM] sampling points were completed. For each groundwater sampling point a SCAPS HS analysis was completed and a corresponding sample was collected for analysis by EPA Method 8260B. Groundwater sampling points were located near existing monitoring wells MW107A, MW109A, and MW70 and at 22 other locations.   Sample results were reported for TCE, DCE, benzene, toluene, and total xylenes. In the samples near the three monitoring wells, the primary constituents detected were TCE and DCE. At the other locations only benzene, toluene, and xylenes were detected. The sampling procedure described in Section 6.0 was followed with no reported deviations to the sampling procedure.

The results for the demonstration are summarized in Table 7 below. Regression analysis for each analyte is presented in Figure 12.

TCE concentrations ranged from non-detect to 913 µg/L where 22 data points had concentrations below the detection limit, 1 data points were between 5 µg/L and 100 µg/L, and 9 data points were greater than 100 µg/L. No false positives or false negatives were reported for this analyte. Correlation of the SCAPS HS method and reference method results was good (R^2>0.9).

DCE concentrations ranged from non-detect to 3,451 µg/L where 25 data points had concentrations below the detection limit, 3 data points were between 5 µg/L and 100 µg/L, and 4 data points were greater than 100 µg/L. No false positives were associated with this analyte but false negatives were

9%. The percentage of false positives and negatives ranged from 0% to 9% for the individual studies. The three false negatives were reported at 24.3 µg/L (FD70H01A), 19.5 µg/L (FD70H02A), and 30.2 µg/L(FD70H03A) by the reference method and as non-detect by SCAPS HS. Correlation of the SCAPS HS method and reference method results was good (R^2>0.9).

Benzene concentrations ranged from non-detect to 8,575 µg/L where 20 data points had concentrations below the detection limit, 4 data points were between 5 µg/L and 100 µg/L, and 8 data points were greater than 1000 µg/L. No false positives were associated with this analyte but false negatives were 6%. The two false negative results for benzene were 4µg/L versus 14µg/L (sample FDWTH05) and non-detect versus 5.4µg/L (FDWTH06), respectively. For sample FDWTH05, the false negative for benzene might be counted as a true positive since the SCAPS HS reported an estimated value instead of listing it as non-detect. By counting this sample as a true positive, then the false negatives for benzene would meet the 5% performance criteria. Correlation of the SCAPS HS method and reference method results was poor (R^2=0.7).

Toluene concentrations ranged from non-detect to 20,112 µg/L where 22 data points had concentrations below the detection limit, 2 data points were between 5 and 100 µg/L, and 8 data points were greater than 1000 µg/L. No false positives or false negatives were associated with this analyte. Correlation of the SCAPS HS method and reference method results was poor (R^2=0.7).

Xylenes concentrations ranged from non-detect to 13,758 µg/L where 20 data points had concentrations below the detection limit, 2 data points were between 5 µg/L and 100 µg/L, and 10 data points were greater than 100 µg/L. False positives and false negatives were 3%. The false positive is associated with sample FDDSH03 where the SCAPS HS method reported a value of 300 µg/L and the reference method a value of non-detect. The false negative was reported for sample FDWTH05 where the reference method reported 133.6 µg/L and the SCAPS HS method reported non-detect. Correlation of the SCAPS HS method and reference method results was poor (R^2=0.6).

Analytes	Number of GW Samples		Sample Result Distribution				r^2	Detection Limit (ng/mL)		EPA Method 8260 Confirmation Sample Max. Conc. (ng/mL)	true +		true -		false +		false -	
	Hydrosparge	Confirmation	n<5	5<n<100	100<n<1000	n>1000		Method 8260	Hydrosparge		Number	%	Number	%	Number	%	Number	%
TCE	32	32	22	1	9	0	1.0	<5	<5	913	7	22%	25	78%	0	0%	0	0%
DCE			25	3	2	2	1.0	<5	<5	3451	4	13%	25	78%	0	0%	3	9%
BENZENE			20	4	0	8	0.7	<5	<5	8575	10	31%	20	63%	0	0%	2	6%
TOLUENE			22	2	0	8	0.7	<5	<5	20112	11	34%	21	66%	0	0%	0	0%
XYLENES			20	2	1	9	0.6	<5	<5	13758	10	31%	20	63%	1	3%	1	3%

Three samples analyzed by the SCAPS HS and by the WES ECB Laboratory were also analyzed by PDP, an independent laboratory. A comparison of these results is shown in Table 8. While there are insufficient data points with each analyte to perform a regression analysis, it appears that the results for the three methods are comparable.

Sample	TCE (µg/L)			DCE (µg/L)			Benzene (µg/L)			Toluene (µg/L)			Xylenes (µg/L)		
	HS[1]	ECB[2]	PDP[3]	HS	ECB	PDP	HS	ECB	PDP	HS	ECB	PDP	HS	ECB	PDP
FDTSH01	0	0	0	0	0	0	2700	7600	3000	7000	17700	6000	6500	8567	6800
FDTSG01	0	0	0	0	0	0	1200	3600	5100	1400	5600	9300	3000	4900	9800
FD107AH4	310	330	310	2280	2900	3400	0	0	0	0	0	0	0	0	0

1 - SCAPS Hydrosparge/Ion Trap Mass Spectrometry

2 - Environmental Chemistry Branch, Waterways Experimental Station, U.S. Army Corp of Engineers Method 8260

3 - PDP Laboratory, an Independent Laboratory.

7 DISCUSSION

7.1 Summary of Results

Results for all six field studies were combined into one data set and plotted by analyte. Figures 13 and 14 present the linear regression results for the pooled data by analyte. These results are discussed in the paragraphs below.

TCA results were available only for the Building 525 field study conducted at the Aberdeen Proving Grounds. Twenty three samples were analyzed using the SCAPS HS and the reference method, EPA Method 8260B. TCA concentrations ranged from non-detect (< 5 µg/L) to 1300 µg/L where 7 data points had concentrations below the detection limit, 11 data points were between 10 and 100 µg/L, and 5 data points were greater than 100 µg/L. The percentage of false positives was 9% (or 2 out of 23 samples) while the false negatives were 4% (or 1 out of 23 samples). The small number of samples makes this of limited statistical value because a small number of false positives or negatives can result in failure to meet the criteria. Comparison of SCAPS HS method to the reference method results were good (R^2=0.98) even though the number of data points were limited.

DCE results were based on data from field studies at the NAS Whiting Field, MMR, Fort Dix, and DGCS. A total of 84 samples were analyzed using the SCAPS HS and EPA Method 8260B. DCE concentrations ranged from non-detect to 3,451 µg/L where 58 data points had concentrations below the detection limit, 22 data points were between 5 µg/L and 100 µg/L, and 4 data points were greater than 100 µg/L. The percentage of false positives ranged from 0 to 9% and false negatives from 0% to 11% for the individual studies. Data pooled from five field studies yielded 1% false positives and 7% false negative. The correlation between the field results and the reference method was good when the data was pooled (R^2>0.9). One field study conducted at the DGCS yielded a poor correlation (R^2=0.4) but there was insufficient information to determine which factors contributed to the lower correlation.

TCE results were based on data collected at the Aberdeen Proving Grounds (Building 525 and the BRSA), NAS Whiting Field, MMR, Fort Dix, and DGCS. A total of 189 samples were analyzed using

the SCAPS HS and EPA Method 8260B. TCE concentrations ranged from non-detect to 1,200 µg/L where 105 data points had concentrations below the detection limit, 47 data points were between 5 µg/L and 100 µg/L, and 37 data points were greater than 100 µg/L. TCE results had false positives between 0% to 13% and false negatives between 0% to 11%. When the data for the eight field studies were pooled, the pooled data yielded 3% false positives, 5% false negatives, and a good correlation coefficient (R^2=0.8). Correlation coefficients for five of the eight field studies were good (R^2>0.8). For one field study, there was insufficient data to perform a regression analysis. For two demonstrations, the correlation was poor although other demonstrations conducted at the same locations (DGCS and BRSA) yielded data with good correlation (R^2>0.8).

Data for DCE/TCA mixtures were based on the field studies conducted at the BRSA at the Aberdeen Proving Grounds. A total of 82 samples were analyzed using the SCAPS HS and EPA Method 8260B. DCE/TCA concentrations ranged from non-detect to 159 µg/L where 68 data points had concentrations below the detection limit, 12 data points were between 5 µg/L and 100 µg/L, and 2 data points were greater than 100 µg/L. The percentage of false positives was 5% and false negatives ranged from 3% to 5%. Correlation of the data with the reference method was poor for both the individual field studies and the pooled data (R^2≤0.6).

Data for 1,1,2,2-tetrachloroethane and chloroform (1,1,2,2/CHCL3) mixtures were based on the field studies conducted at the BRSA at the Aberdeen Proving Grounds, and the MMR. A total of 93 samples were analyzed using the SCAPS HS and EPA Method 8260B. 1,1,2,2/CHCL3 concentrations ranged from non-detect to 8,970 µg/L where 40 data points had concentrations below the detection limit, 27 data points were between 5 µg/L and 100 µg/L, and 26 data points were greater than 100 µg/L. False positives for 1,1,2,2/CHCL3 ranged from 2% to 16%, and from 16% to 21% for false negatives. Correlation of the data with the reference method were poor for the individual field studies and pooled data (R^2<0.6). The low correlation coefficient may be due to the large number of false negatives where the reference method reported concentrations lying outside the ITMS calibration curve. In addition, the different relative response for a mixture of two chemicals may contribute to the low correlation coefficient.

CCl$_4$ results were based on data collected at the Bush River Study Area at the Aberdeen Proving Grounds, and the MMR. A total of 93 samples were analyzed using the SCAPS HS and EPA Method 8260B. CCl$_4$ concentrations ranged from non-detect to 590 µg/L where 71 data points had concentrations below the detection limit, 15 data points were between 5 µg/L and 100 µg/L, and 7 data points were greater than 100 µg/L. CCl$_4$ results had false positives ranging from 0% to 5% and false negatives ranging from 0% to 3%. Data correlation between the field results and the reference method varied from poor (R^2=0.2) to good (R^2=0.9) at the same site between field studies. Insufficient information was available to identify potential causes for these differences. When the data was pooled, a good correlation (R^2=0.8) was observed between the field results and the reference method.

PCE results were based on data collected at the Bush River Study Area at the Aberdeen Proving

Grounds, NAS Whiting Field, MMR, and the DGCS. A total of 134 samples were analyzed using the SCAPS HS and EPA Method 8260B. PCE concentrations ranged from non-detect to 820 µg/L where 95 data points had concentrations below the detection limit, 27 data points were between 5 µg/L and 100 µg/L, and 12 data points were greater than 100 µg/L. For the individual field studies, false positives varied from 0% to 16% and false negatives from 0% to 9%. Pooled PCE data yielded false positives and negatives at 4%. A review of the field data associated with the 16% false positive field study found the elevated number may be due to a size of the data set (19 points). Correlation between the field results and reference method results for individual field studies were poor ($0.0 < R^2 < 0.6$) except for one field study where the correlation was good ($R^2 = 1.0$). Due to the limited amount of information available, the cause for the low correlation was not identified. The pooled data for PCE also correlated poorly ($R^2 = 0.6$) and may be due to a single data point which OPPTD staff were unable to determine if it was an outlier.

Benzene results were based on data collected at Fort Dix, NAS Whiting Field, and MMR. A total of 52 samples were analyzed using the SCAPS HS and EPA Method 8260B. Benzene concentrations ranged from non-detect to 8,575 µg/L where 40 data points had concentrations below the detection limit, 4 data points were between 5 µg/L and 100 µg/L, and 8 data points were greater than 1000 µg/L. Benzene data had false positives below 5% while the false negative percentages ranged from 0% to 6%. For two field studies, correlations for benzene were poor ($R^2 \leq 0.7$). No correlations were calculated at the third site since concentrations were reported below the detection limit. Field results correlated well ($R^2 = 0.8$) with the reference method results when the data was pooled.

Data for toluene were based on data collected at Fort Dix, NAS Whiting Field, and MMR. A total of 52 samples were analyzed using the SCAPS HS and EPA Method 8260B. Toluene concentrations ranged from non-detect to 20,112 µg/L where 41 data points had concentrations below the detection limit, 3 data points were between 5 and 100 µg/L, and 8 data points were greater than 1000 µg/L. Toluene data had false positives and false negatives below 5% for the individual field studies. For one field study, the field results and reference method results for toluene correlated poorly ($R^2 \leq 0.7$) while another site showed good correlation ($R^2 = 0.9$). Pooled data between the field results and the reference method correlated poorly ($R^2 = 0.7$). This appears to be due to a single data point which OPPTD staff were unable to determine if it was an outlier.

Xylenes results were based on data collected at Fort Dix, NAS Whiting Field, and MMR. A total of 52 samples were analyzed using the SCAPS HS and EPA Method 8260B. Xylenes concentrations ranged from non-detect to 13,758 µg/L where 40 data points had concentrations below the detection limit, 2 data points were between 5 µg/L and 100 µg/L, and 10 data points were greater than 100 µg/L. Xylenes had false positives and false negatives below 5% for the individual field studies. For one field study, xylenes field results correlated poorly with the reference method results ($R^2 \leq 0.7$). Linear correlation analyses were not performed for the other two studies due to insufficient data. Field results were found to correlate poorly ($R^2 = 0.6$) with the reference method results even when individual field study data were pooled.

7.2 Other Factors in Data Interpretation

Several other factors were also considered in the interpretation of the data presented above. One of these factors was the data distribution. For four of the eight field studies reviewed, the data consisted of less than 20 points where one false positive or negative would cause the percentage of false positives or negatives to exceed 5%. For all the field studies, the pooled data for each analyte contained a large number of data points where the concentration was below the detection limit. With the large number of data points grouped near the origin, the data distributed at higher concentrations were shown to have a greater influence on the correlation coefficient.

Another factor considered was the technology's inability to produce consistent results for a specific analyte at the same location. This was illustrated in the differing correlations presented for demonstrations conducted at the DGCS and the Aberdeen Proving Grounds BRSA. Since field notes on operator field activities and site conditions were not available in the summary reports, OPPTD staff were unable to assess potential effects of various parameters on the results. Differences in the consistency of the SCAPS HS method to report groundwater concentrations between demonstrations could be due to site conditions, personnel operating the SCAPS HS and ITMS, helium flow rate used in well sparging, and equipment cleaning and calibration methods used. These factors may contribute to inconsistent results for the same site between demonstrations.

From the interlaboratory comparison data for DGCS and Fort Dix, it appears that the SCAPS HS results and the reference results are as comparable to each other as the reference method results from the two laboratories. However at DGCS for concentrations greater than 200 µg/L, the reference method results for ECB and the independent laboratory differed greatly although the SCAPS HS results and reference method results from ECB were in closer agreement.

7.3 Conclusions

The Hydrosparge VOC Sensor (HS) of the Site Characterization and Analysis Penetrometer System (SCAPS) and Direct Sampling Ion Trap Mass Spectrometer (ITMS) was demonstrated to be a near real-time in-situ field screening method for trichloroethene (TCE), benzene, carbon tetrachloride, perchloroethylene (PCE), dichloroethene (DCE), toluene, and xylenes in groundwater. The technology was demonstrated to be a qualitative to semi-quantitative field screening method for TCE, benzene, and carbon tetrachloride and met the criteria of less than 5% false positives and negatives and had good correlation ($R^2 \geq 0.80$). For PCE, toluene, and xylenes, the technology was demonstrated to be a qualitative field screening method and met the criteria of less than 5% false positives and negatives but had lower correlations ($R^2 < 0.80$). For DCE, the technology was demonstrated not to meet the criteria of less than 5% false negatives but had good correlation ($R^2 \geq 0.80$) and could be a qualitative field screening method for this analyte.

The performance data obtained using the SCAPS HS were comparable to the U.S. EPA Method 8260B for the analytes listed above. Performance data for analyte mixtures were not comparable since the ITMS does not have a separation mechanism other than the mass spectrometer. Compounds which produce identical primary characteristic ions, or positional and geometric isomers (e.g., 1,1-dichloroethene and 1,2-dichloroethene), could not be positively identified when a characteristic secondary ion is not available for monitoring. Compounds with higher molecular weights (e.g., 1,1,2,2-tetrachloroethane) might produce the same fragment ions (e.g., chloroform) which would increase the signal of target analytes.

With an established 5 point linear calibration curve ($R^2 \geq 0.95$), the technology typically estimated the concentrations of individual VOC analytes in groundwater at concentrations down to a detection limit of 5 µg/L. The correlation between VOC results obtained from a temporary direct push sampling point used to access groundwater with that obtained by EPA Method 8260B varied depending on the specific constituents and the site.

Since this technology can only detect or confirm the presence of known specific contaminants, confirmation samples should be collected for each SCAPS HS sample until the technology has been demonstrated to be effective in sparging the contaminants of concern at a specific site. In addition, matrix effects and even the particular contaminant or contaminants present, might vary with depth. It is recommended that confirmation groundwater samples be collected at the same depth as the SCAPS HS analyses. The depth and size of the contaminant plume, and contamination profile of a site should all be considered in a site-specific sampling plan for determining the necessary number and locations of confirmation samples once the technology is proven effective for the contaminants of concern. Site characterization data obtained during prior investigations should also be considered.

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APPENDIX A
Field Test Data by Demonstration Study

Appendix B
Figures